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Thermodynamic Properties and Moisture Sorption Isotherms of *Argania spinosa* and *Zygophyllum gaetulum*

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Abstract: Almond of *Argania spinosa* and *Zygophyllum gaetulum* moisture sorption isotherms were determined within the range of 0.1-0.9 water activity at three temperatures (30, 40 and 50°C), using saturated salt solutions dynamic method. Sorption isotherms of *Argania spinosa* and *Zygophyllum gaetulum* have, respectively a sigmoid shape (Type 2) and (Type 5). The GAB, modified Oswin, modified Henderson, Peleg, modified BET and modified Halsey models were tested to fit the experimental data. In relation to the isotherm models the best models were, GAB, modified Oswin and Peleg obtaining minor values of % mean relative errors and higher correlation coefficient. Isosteric heats of sorption were calculated through direct use of moisture isotherms by applying the Clausius-Clapeyron equation. The differential enthalpy and entropy decreased with increasing moisture content and were adequately characterized by polynomial function. A plot of differential heat versus entropy satisfied the enthalpy-entropy compensation theory. The comparison between the sorption isotherms and thermodynamic properties of *A. spinosa* almond and *Z. gaetulum* was studied.

Key words: *Argania spinosa*, food storage, sorption isotherms, thermodynamic properties *Zygophyllum gaetulum*

INTRODUCTION

The medicinal and aromatic plants have a great importance for both the pharmaceutical industry and the traditional medicine in Arab Maghreb countries (Kouhila *et al*., 2001). The *A. spinosa*, family of *Sapotacee*, is a localized endemic forest gasoline in the South-west of Morocco. This tree forester-fruit-loft is a botanical curiosity and a true phytogeographical paradox. The Moroccan traditional pharmacopoeia uses oil extracted from *Argania spinosa* almond to treat acne, alopecia, eczema and irritations. Its foliage is used for its inflammatory anti properties to treat particular rheumatism, pains and earaches (Berrougui *et al*., 2003; Charrouf *et al*., 1992; Charouf and Dominique, 1999).

Z. gaetulum (healer plant) belongs to the family of *Zygophyllaceae* with branching small sheets made up of two fleshy leaflets used as water reserve. *Z. gaetulum* pushes resolutely in the ergs. In Moroccan traditional pharmacopoeia, *Z. gaetulum* is indicated for its antidiabetic properties (Tahraoui *et al*., 2007). A recent study highlighted its hypoglycemia activity (Jaouhari *et al*., 2000).

Studies in processing and physical properties behaviour are scarce in literature, such as sorption isotherm data of these plants that it is of fundamental importance in the dimensionally of packing, equipment and storage for industrialization in commercial scale (Kouhila *et al*., 2001; Krokida *et al*., 2000).

Water activity (a_w) is important to determine the stability criteria for foodstuffs and it is function of the equilibrium moisture content and the temperature. In this way, microbial growth, browning, lipid oxidation and other physical properties (colour, texture, flavour, etc.) are dependent of water activity of the product (Ait Mohamed *et al*., 2005a, b; Jamali *et al*., 2006a; Lahsasni *et al*., 2004). Sorption isotherms are important to improve the conditions of several processes such as dehydration, packing or storage (Ait Mohamed *et al*., 2005b; Kouhila *et al*., 2002; Lahsasni *et al*., 2002; Vazquez *et al*., 2001).

The experimental sorption data are fitted with six mathematical equations. These equations are theoretical (BET and GAB models), semi-theoretical (Henderson and Halsey models) or empirical (Oswin and Peleg). Some equations have a dependent temperature term and

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were used to reflect the temperature dependency of moisture sorption isotherms. Each of the suggested equations has some success in describing sorption isotherms for a given type of product according to the Brunauer classification. The GAB equation is considered as the most model suitable to be applied to many products types and over a wide range of water activity. However, there is actually, no perfect equation for describing sorption isotherms for all biological materials (Bizot, 1983; Chirife and Iglesias, 1978; Jamali *et al.*, 2006b; Kaya and Kahyaoglu, 2007).

Thermodynamic properties such as the net isosteric heat of sorption could be deduced from sorption isotherms and could be used to estimate the energy requirements for the dehydration process. The energy required to dehydrate or rehydrate the product could be thus determined. The isosteric heat of sorption and the equilibrium moisture content could be used to analyse and design different food processes. Sorption isotherms could be also used for fundamental investigations such as the study of the moisture-solid interactions (Chirife and Iglesias, 1978). The level of material moisture content at which the net isosteric heat of sorption approaches the latent heat of vaporisation of water is often taken as an indication of the amount of bound water existing in the food (Henderson, 1952; Van Den Berg and Bruin, 1981).

The objectives of the present study are to determine the water sorption isotherms of *A. spinosa* almond and *Z. gaetulum* at 30, 40 and 50°C; to fit the experimental data using six sorption models and to determine the thermodynamic properties (isosteric heats of sorption, differential enthalpy and differential entropy).

MATERIALS AND METHODS

Almond of *Argania spinosa* and *Zygophyllum gaetulum* used for the sorption experiments, were grown in the regions of Tiznit and Errachidia regions respectively (south of Morocco) and got from the local market in June 2006 (Fig. 1). The study was conducted in The Laboratory of Solar Energy and Medicinal Plants, Cadi Ayyad University of Marrakech (Morocco).

Adsorption and desorption method: The methodology used to obtain the equilibrium data was based on the dynamic method with saturated salt solutions. The salts were chosen, to obtain a large range of water activity. The equilibrium moisture contents of *Z. gaetulum* and *A. spinosa* almond were determined by a gravimetric technique, in which the weigh changes were monitored continuously within a dynamic system

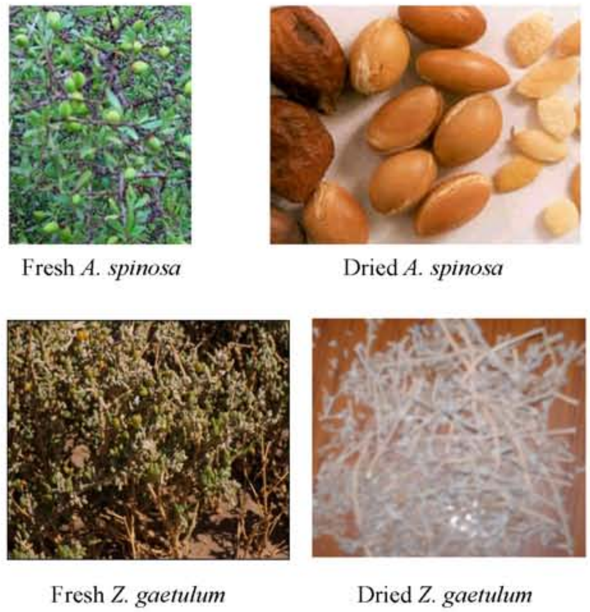

Fig. 1: Fresh and dried *A. spinosa* and *Z. gaetulum*

Table 1: Selected saturated salt solutions and corresponding water activities

	Water activity (a_w)		
Salt	30°C	40°C	50°C
KOH	0.0 738	0.0626	0.0572
$MgCl_2 . 6H_2O$	0.3238	0.3159	0.3054
K_2CO_3	0.4317	0.4230	0.4091
$NaNO_3$	0.7275	0.7100	0.6904
KCl	0.8362	0.8232	0.8120
$BaCl_2 . 2H_2O$	0.8980	0.8910	0.8823

of thermally stabilized (30, 40 and 50°C). Although this method requires a long time for the hygroscopic equilibrium to be attained, it has the advantage of presenting a more restricted domain of moisture content variation (Jamali *et al.*, 2006b).

Fresh plants were used in the desorption experiments. Samples used in the adsorption isotherms were dried in an oven regulated at 50°C until reaching maximum dehydration (Fig. 1).

Six salts (KOH, ($MgCl_2 . 6H_2O$), K_2CO_3, $NaNO_3$, KCl and ($BaCl_2 . 2 H_2O$) were chosen so as to have a range of water activity from 0.05 to 0.9. Table 1 shows the standard values of water activities given for the six salts as a function of temperature.

Description of experimental procedure: The experimental apparatus is shown in Fig. 2. It consists of six glass jars of 1l each with an insulated lid. Every glass jar is filled to quarter depth with a saturated salt solution. Each glass jar contains a different salt solution.

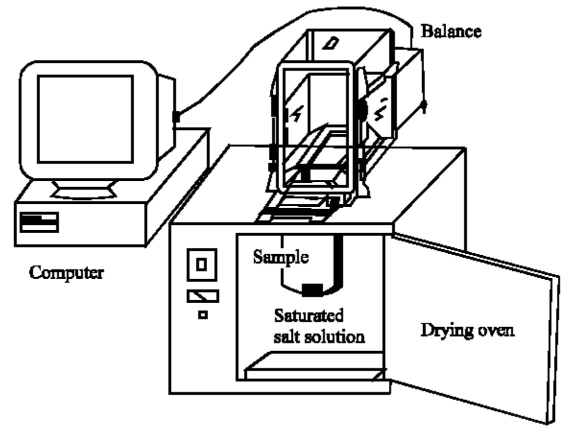

Fig. 2: Experimental apparatus for measurement of sorption isotherms

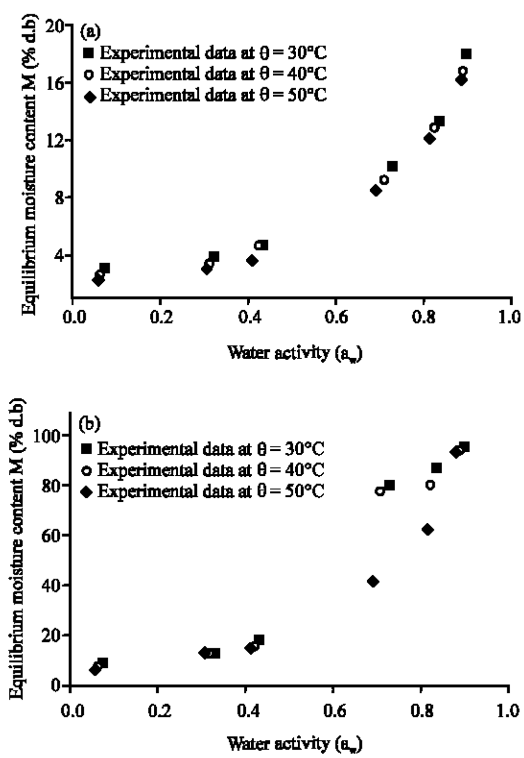

Fig. 3: Influence of temperature on the desorption isotherms of (a) *A. spinosa* and (b) *Z. gaetulum*

The glass jars are immersed in an oven adjusted to a fixed temperature for 24 h so as to bring the salt solutions to a stationary temperature. The weight recording period was about 4 days. This procedure was continued until the weight was constant. The moisture content of each sample was determined by a drying oven whose the temperature was fixed at 105°C.

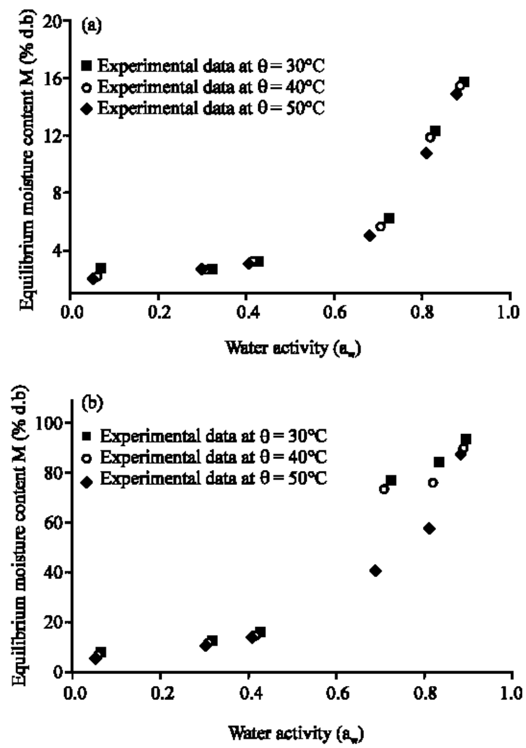

Fig. 4: Influence of temperature on the adsorption isotherms of (a) *A. spinosa* and (b) *Z. gaetulum*

The difference of mass before and after drying in the oven determines the moisture content of the product at hygroscopic equilibrium. The results of these experiments are shown in Fig. 3-4.

Modelling of the sorption isotherms: The adsorption and desorption experimental data were analysed by using six mathematical equations chosen among the most used in literature (Kouhila *et al.*, 2002; Lahsasni *et al.*, 2004; Lomauro *et al.*, 1985). The isotherm equations used to fit the data are presented in Table 2. Nonlinear regression analysis, using the computer programs Curve Expert 3.1 and Origin 6.1, was used to estimate the constants of the models from the experimental sorption data for two products.

The suitability of the equations has been evaluated and compared between them using the correlation coefficient (r), the mean relative error MRE (%) and the mean squares of error MSE (Ajibola *et al.*, 2003; Chen and Morey, 1989). These statistical parameters were defined as follows:

$$\mathrm{MRE} = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{M_{ie} - M_{ip}}{M_{ie}}\right| \qquad (1)$$

Table 2: Mathematical equations used to describe the sorption isotherms

Model	Equation	Reference
GAB	$M=\frac{ABCa_w}{[1-Ba_w]\,[1-Ba_w+BCa_w]}$ $B=B_0\exp\left(\frac{h_1}{RT}\right)$ and $C=C_0\exp\left(\frac{h_2}{RT}\right)$	Van Den Berg and Bruin (1981)
Modified Oswin	$M=(A+B\theta)\left[\frac{a_w}{1-a_w}\right]^C$	Oswin (1946)
Modified Henderson	$1-a_w=\exp\left[-A(\theta+B)M^C\right]$	Thompson *et al.* (1986)
Peleg	$M=Aa_w^C+Ba_w^D$	Peleg (1993)
Modified BET	$M=\frac{(A+B\theta)Ca_w}{(1-a_w)\,(1-a_w+Ca_w)}$	Brunauer *et al.* (1938)
Modified Halsey	$a_w=\exp\left[\frac{-\exp(A+B\theta)}{M^C}\right]$	Chirife and Iglesias (1978)

$$MSE=\sqrt{\frac{\sum_{i=1}^{N}\left(M_{ie}-M_{ip}\right)^2}{d_f}} \quad (2)$$

Where:
N = Numner of data points
d_f = Number of degrees of freedom

Isosteric heat of sorption: The isosteric heat of sorption (ΔH_d), or differential enthalpy, is an indicator of the state of water absorbed by the solid material. The net isosteric heat of sorption (Δh_d) is the amount of energy above the heat of vaporization of water (ΔH_{vap}) associated with the sorption process and was calculated from the experimental data using the Clausius-Clapeyron equation (Kaymak-Ertekin and Gedik, 2004; Tsami, 1991):

$$\left[\frac{d(\ln a_w)}{d\left(\frac{1}{T}\right)}\right]_M=\frac{-\Delta h_d}{R} \quad (3)$$

and

$$\Delta h_d=\Delta H_d-\Delta H_{vap} \quad (4)$$

It is a differential quantity, the value of which corresponds to sorbed molecules at particular equilibrium moisture content (M).

Integrating Eq. 3, assuming that the net isosteric heat of sorption (Δh_d) is temperature independent gives the following equation:

$$\ln(a_w)=-\left(\frac{\Delta h_d}{R}\right)\frac{1}{T}+Cste \quad (5)$$

Re-plotting the experimental sorption isotherm in the form $\ln(\alpha_w)$ versus $\frac{1}{T}$, for specific equilibrium moisture content, Δh_d was determined from the slop

$$\left(\frac{-\Delta h_d}{R}\right).$$

This procedure is based on the assumption that ΔH_d is invariant with temperature and requires measurement of the sorption isotherms at more than two temperatures (Tsami, 1991).

Enthalpy-entropy compensation theory: The relationship between the net isosteric heat (Δh_d) and the differential entropy of sorption (ΔS_d) is given by:

$$(-\ln a_w)_M=\frac{\Delta h_d}{RT}-\frac{\Delta S_d}{R} \quad (6)$$

By plotting $\ln(\alpha_w)$ versus $\frac{1}{T}$, for a given moisture content (M), Δh_d was determined from the slope

$$\left(\frac{-\Delta h_d}{R}\right)$$

and ΔS_d from the intercept

$$\left(\frac{\Delta S_d}{R}\right).$$

Applying this at different moisture contents allowed the dependence of Δh_d and ΔS_d with moisture to be determined (Aguerre *et al.*, 1986).

The compensation theory proposes a linear relationship between Δh_d and ΔS_d (Leffer and Grunwald, 1963; McMinn and Magee, 2003):

$$\Delta h_d = T_\beta.\Delta S_d + \alpha \qquad (7)$$

The isokinetic temperature (T_β) and constant (α) were calculated using linear regression.

RESULTS AND DISCUSSION

Adsorption and desorption isotherms: *A. spinosa* and *Z. gaetulum* used in the sorption isotherms experiments were grown in the Tiznit and Errachidia regions respectively (South of Morocco). The hygroscopic equilibrium of *Z. gaetulum* is reached in 34 days and *A. spinosa* in 17 days. The results of the experimental adsorption and desorption equilibrium moisture contents of the two plants at three temperatures are given in Table 3 and 4. It can be seen from Fig. 3-4 that the sorption isotherms of *Z. gaetulum* and *A. spinosa* showed typical sigmoid shape characteristics of food materials with an oil content, which sorbs relatively small amount of water at lower water activities (Iglesias and Chirife, 1982).

Temperature has a significant effect on desorption and adsorption isotherms. The equilibrium moisture contents increase with decrease in temperature at constant water activity. The temperature shifts have an important practical effect on chemical and microbiological reactions related to quality deterioration. An increase of temperature causes an increase of water activity of two products particles at the same moisture content, which causes the reaction rates leading to quality deterioration.

Sorption isotherms ($M = f(\alpha_w)$), of the two plants, obtained by experiment for three temperatures are regrouped in Fig. 5-6. When the hygroscopic equilibrium is reached, the water exchanges between air and the product, attain an equilibrium and the activity of water a_w becomes identical to the equilibrium relative humidity Rh (a_w = Rh (%)/100). The equilibrium moisture content increases with decreasing temperature at constant relative humidity.

By comparing the sorption isotherms of two products at θ = 30 and 40°C, it can be seen that *Argan* almond has a hygroscopic behaviour different from that of *Z. gaetulum*. Figure 5-6 show that at constant relative humidity, the equilibrium moisture content of *Z. gaetulum* is higher than that of *A. spinosa*. This result means that if the storage temperature of a medicinal plant is equal to 40°C, in an ambience whose relative humidity is fixed, *A. spinosa* will be dried to a final moisture content that is lower than *Z. gaetulum*. Figure 7 shows that the sorption hysteresis phenomenon was observed only for *A. spinosa* almond. This is due to the fact that the moisture content of *Argan* almond at wet basis is very weak compared to that of *Z. gaetulum*.

Fitting of sorption models to experimental data: The experimental data of the adsorption and desorption curves of *A. spinosa* almond and *Z. gaetulum* were fitted to six sorption models (Table 2). The coefficients of the models with their correlation coefficient (r), statistic Mean Relative Error (MRE) and Mean Squares of Error (MSE) are presented in Table 5-8.

The GAB, Peleg and modified Oswin models had the highest (r) value and the lowest (MRE) and (MSE) values for desorption and adsorption compared to the other models. These models were found to be the best estimators for predicting the equilibrium moistures of the two plants. At water activity lower than 0.5, the BET model gives the highest (r) equal to the unit and the lowest (MRE) and (MSE) values of desorption and

Table 3: Sorption data of *Z. gaetulum* obtained at different water activities and temperatures

30°C			40°C			50°C		
a_w	des	ads	a_w	des	ads	a_w	des	ads
0.0738	8.2386	7.9412	0.0626	6.8182	6.7308	0.0572	6.2500	5.7143
0.3238	12.8205	12.4762	0.3159	12.8205	11.5385	0.3054	12.8205	10.7872
0.4317	17.7778	16.0377	0.4230	15.5556	14.5631	0.4091	15.3086	14.2857
0.7275	80.0000	77.0892	0.7100	77.5599	73.3204	0.6904	42.0479	40.9135
0.8362	87.0968	84.3721	0.8232	79.7386	75.9420	0.8120	62.3277	57.8431
0.8980	95.0000	93.2296	0.8910	94.4218	89.2925	0.8823	93.3131	88.7081

Table 4: Sorption data of *A. spinosa* almond obtained at different water activities and temperatures

30°C			40°C			50°C		
a_w	des	ads	a_w	des	ads	a_w	des	ads
0.0738	3.1111	2.2901	0.0626	2.6667	2.0305	0.0572	2.22220	2.03050
0.3238	3.9823	2.5381	0.3159	3.5556	2.5253	0.3054	3.18180	2.51260
0.4317	4.6948	3.0612	0.4230	4.6083	3.0457	0.4091	3.65300	3.00000
0.7275	10.1852	6.0000	0.7100	9.2593	5.4726	0.6904	8.41120	5.05050
0.8362	13.1455	12.1212	0.8232	12.8440	11.6751	0.8120	12.0930	10.6599
0.8980	17.8744	15.3846	0.8910	16.6667	15.2284	0.8823	16.1435	14.7208

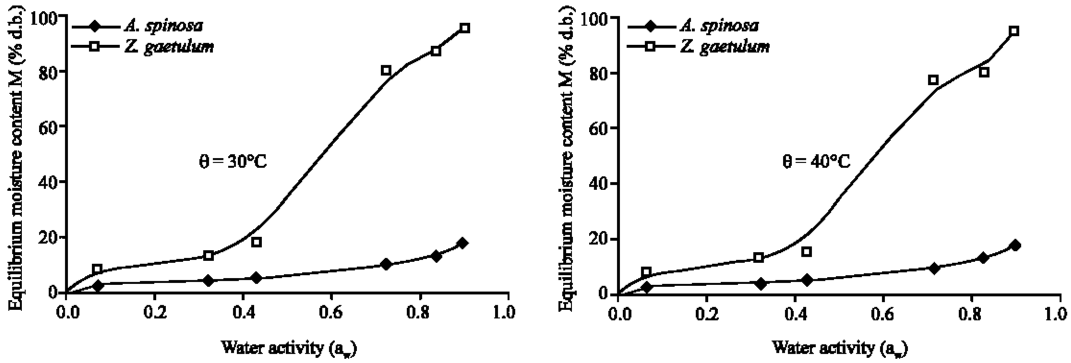

Fig. 5: Comparison of the equilibrium moisture content of desorption of two medicinal plants

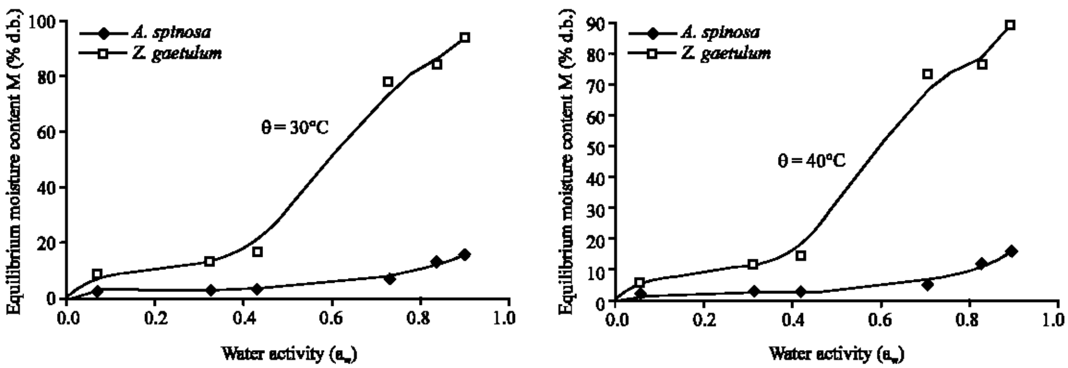

Fig. 6: Comparison of the equilibrium moisture content of adsorption of two medicinal plants

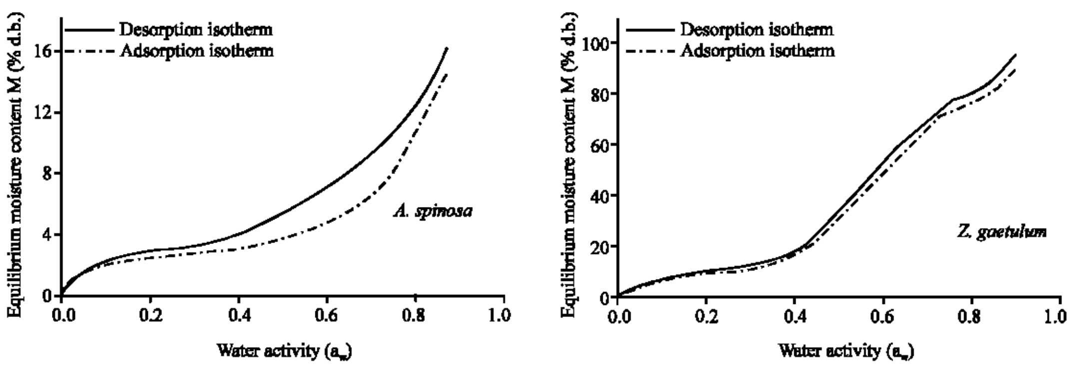

Fig. 7: Thermal hysteresis phenomenon at 50°C

adsorption. The observed and predicted sorption isotherms using the different equations are shown in Fig. 8-11.

Heat of sorption: The values of the isosteric heat of sorption Δh_d were calculated from the equilibrium data at different temperatures using Eq. 5 and obtained at different moisture contents. The variation of the heats of adsorption and desorption of two products with moisture content is shown in Fig. 12-13. The isosteric heats of adsorption and desorption of two products decrease with increase in material moisture content. The heat of desorption is greater than that of adsorption at low moisture contents for all the samples studied. This indicates that energy required in the desorption process is greater than that in the adsorption as stated by Wang and Brennan (1991). Similar results for many plants and foods materials have been reported in the literature (Hossain *et al.*, 2001; McMinn and Magee, 2003; Simal *et al.*, 2007; Stencl *et al.*, 1999;

Table 5: Results of fitting of desorption isotherms of *Z. gaetulum*

	GAB	Modified Oswin	Modified Henderson	Peleg	Modified BET	Modified Halsey
A	17.4373	-11.0276	0.0006	307.9835	-14.8218	4.7256
B		0.6788	51.1213	-186.5865	0.6045	-0.0270
C		1.4371	0.7894	1.5154	32.2875	1.1994
D				1.3358		
B_0	2.0169					
C_0	3.71×10^{-15}					
h_1	-2.0162					
h_2	953.1204					
r	0.9979	0.9983	0.9947	-186.5865	1.00	0.9975
MRE (%)	13.4337	11.9004	19.9325	1.5154	0.0169	9.1706
MSE	2.8840	2.5926	4.5127	1.3358	0.0025	3.0888

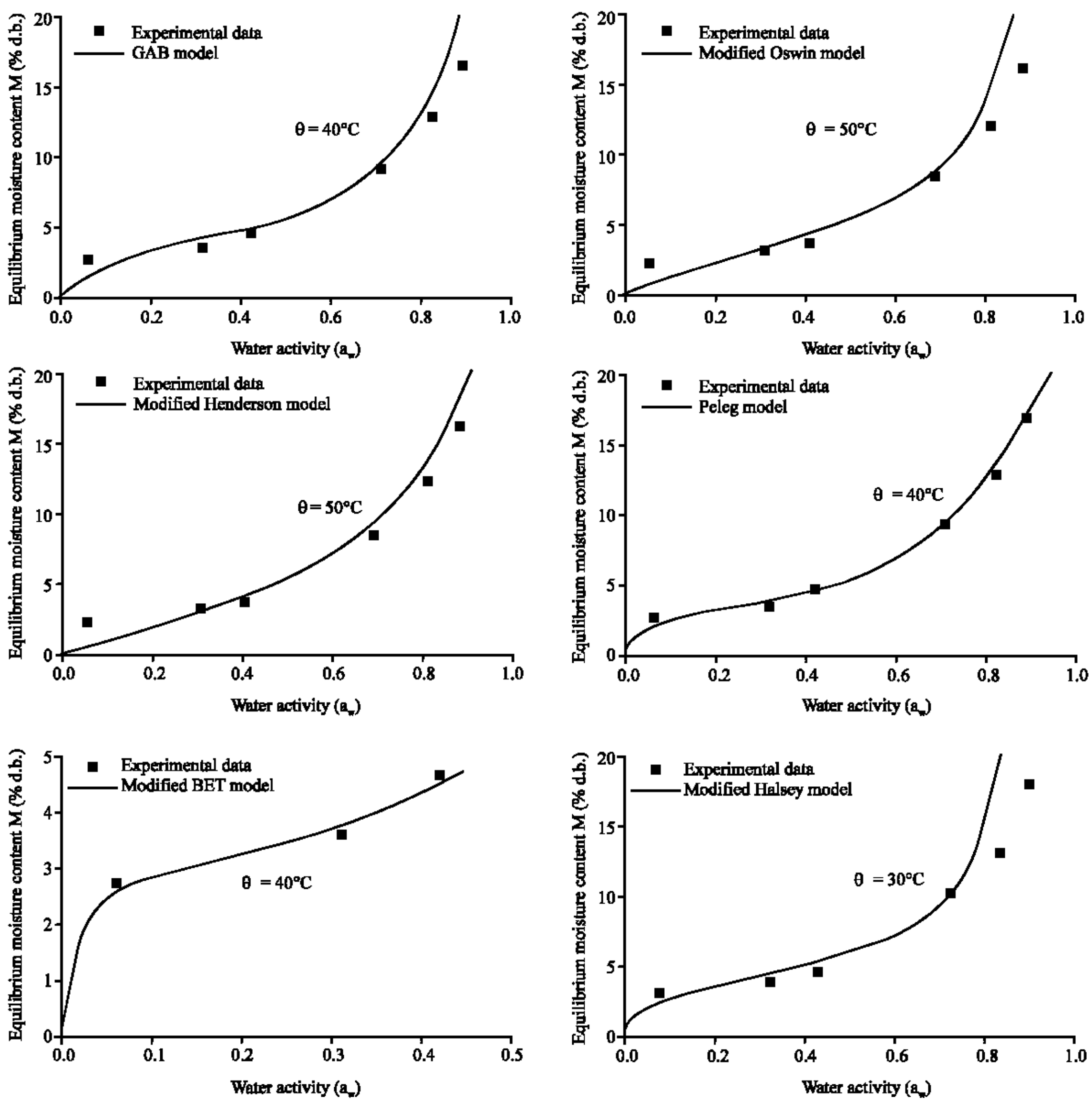

Fig. 8: Comparison of experimental and predicted desorption equilibrium moisture contents of *A. spinosa* fitted by six models

Table 6: Results of fitting of adsorption isotherms of *Z. gaetulum*

	GAB	Modified Oswin	Modified Henderson	Peleg	Modified BET	Modified Halsey
A	16.8248	-10.3293	0.0011	369.7239	-15.2327	2.3738
B		0.6334	7.8711	-250.5525	0.5942	0.0175
C		1.4186	0.7793	1.5385	41.4388	1.1849
D				1.3953		
B_0	1.6787					
C_0	2.4930×10^{-15}					
h_1	-1.5400					
h_2	996.9630					
r	0.9967	0.9972	0.9944	0.9831	1.00	0.9961
MRE (%)	15.7977	14.4129	19.5758	29.1830	1.6864	11.5732
MSE	3.3956	3.1194	4.4334	11.6441	0.2323	3.7240

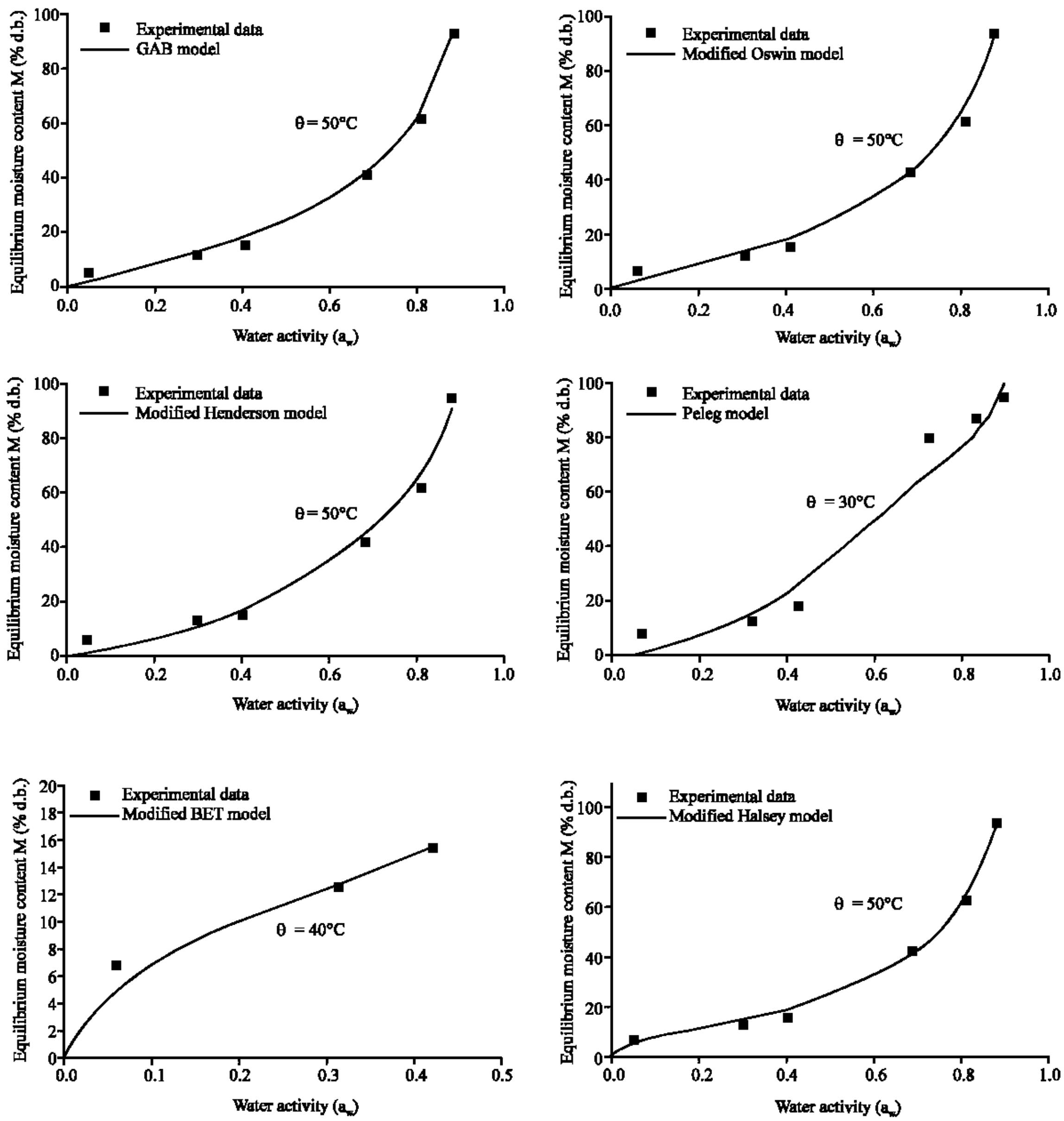

Fig. 9: Comparison of experimental and predicted desorption equilibrium moisture contents of *Z. gaetulum* fitted by six models

Table 7: Estimated values of several model parameters, regression coefficient (r), MRE and MSE for desorption isotherms of *A. spinosa*

	GAB	Modified Oswin	Modified Henderson	Peleg	Modified BET	Modified Halsey
A	3.0229	11.1476	0.0036	4.4960	-17.2103	10.0544
B		-0.1170	-15.4123	19.2056	0.4947	-0.2482
C		1.8013	1.0276	0.1942	390.2176	1.6746
D				3.9943		
B_0	1.2972					
C_0	2.71×10^{-7}					
h_1	-0.8812					
h_2	49.8043					
r	0.9974	0.9945	0.9883	0.9993	1.00	0.9962
MRE (%)	6.6845	12.8025	18.2121	2.8752	3.1387	7.7037
MSE	0.5257	0.7624	1.1083	0.2831	0.1432	0.6672

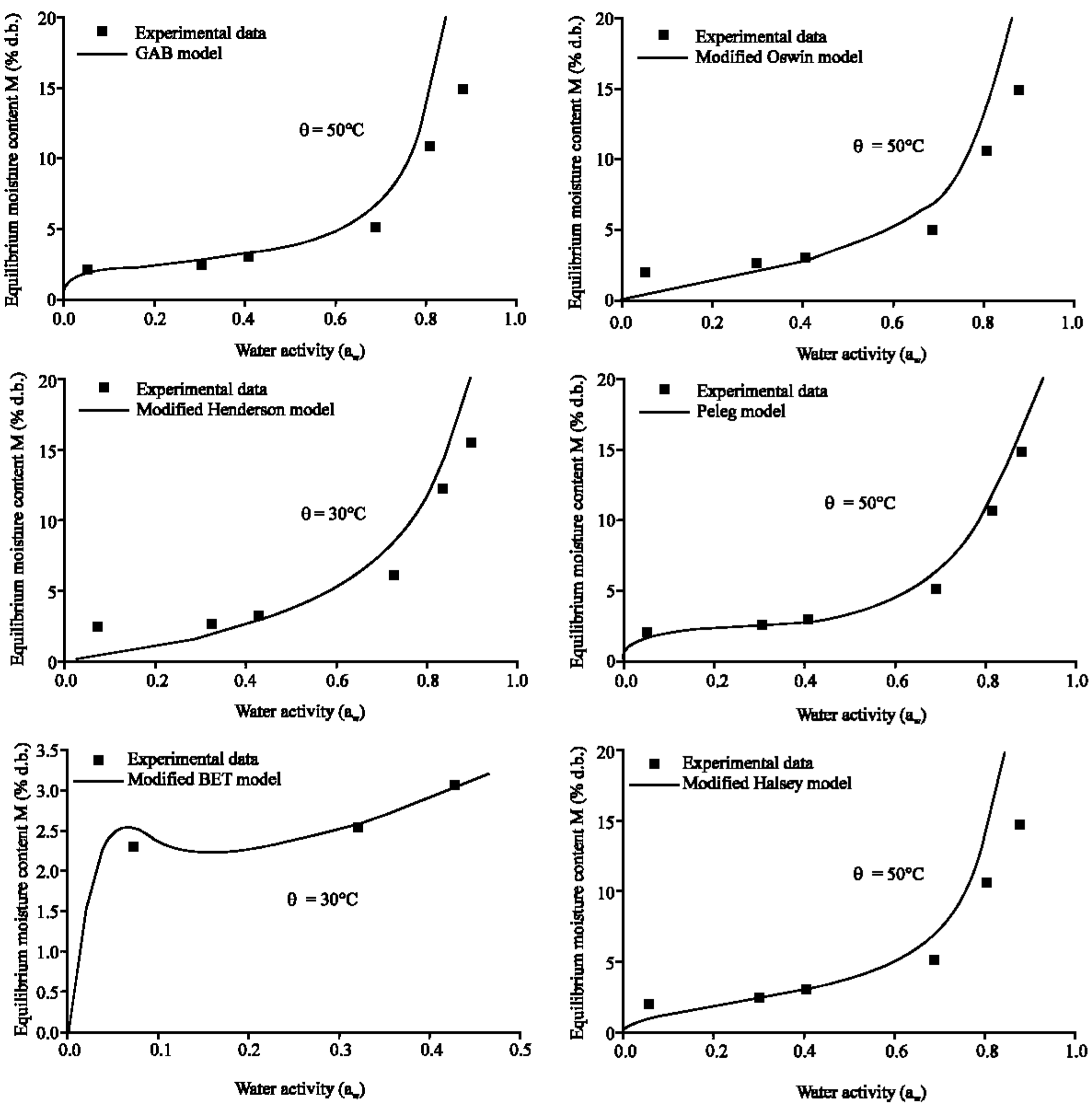

Fig. 10: Comparison of experimental and predicted adsorption equilibrium moisture contents of *A. spinosa* fitted by six models

Table 8: Results of fitting of adsorption isotherms of *A. spinosa* almond

	GAB	Modified Oswin	Modified Henderson	Peleg	Modified BET	Modified Halsey
A	1.9434	3.5985	0.0099	2.9321	-15.1579	7.1289
B		0.0020	-4.9817	25.6101	0.5614	-0.1174
C		1.4609	0.8151	0.1227	-61.1905	1.2358
D				6.0321		
B_0	1.3197					
C_0	1.56×10^5					
h_1	-0.7674					
h_2	-12.1903					
r	0.9926	0.9829	0.9736	0.9977	1.00	0.9900
MRE (%)	7.1316	21.0373	27.4400	4.6186	9.4000	12.9714
MSE	0.8158	1.2348	1.6413	0.4509	0.3390	0.9459

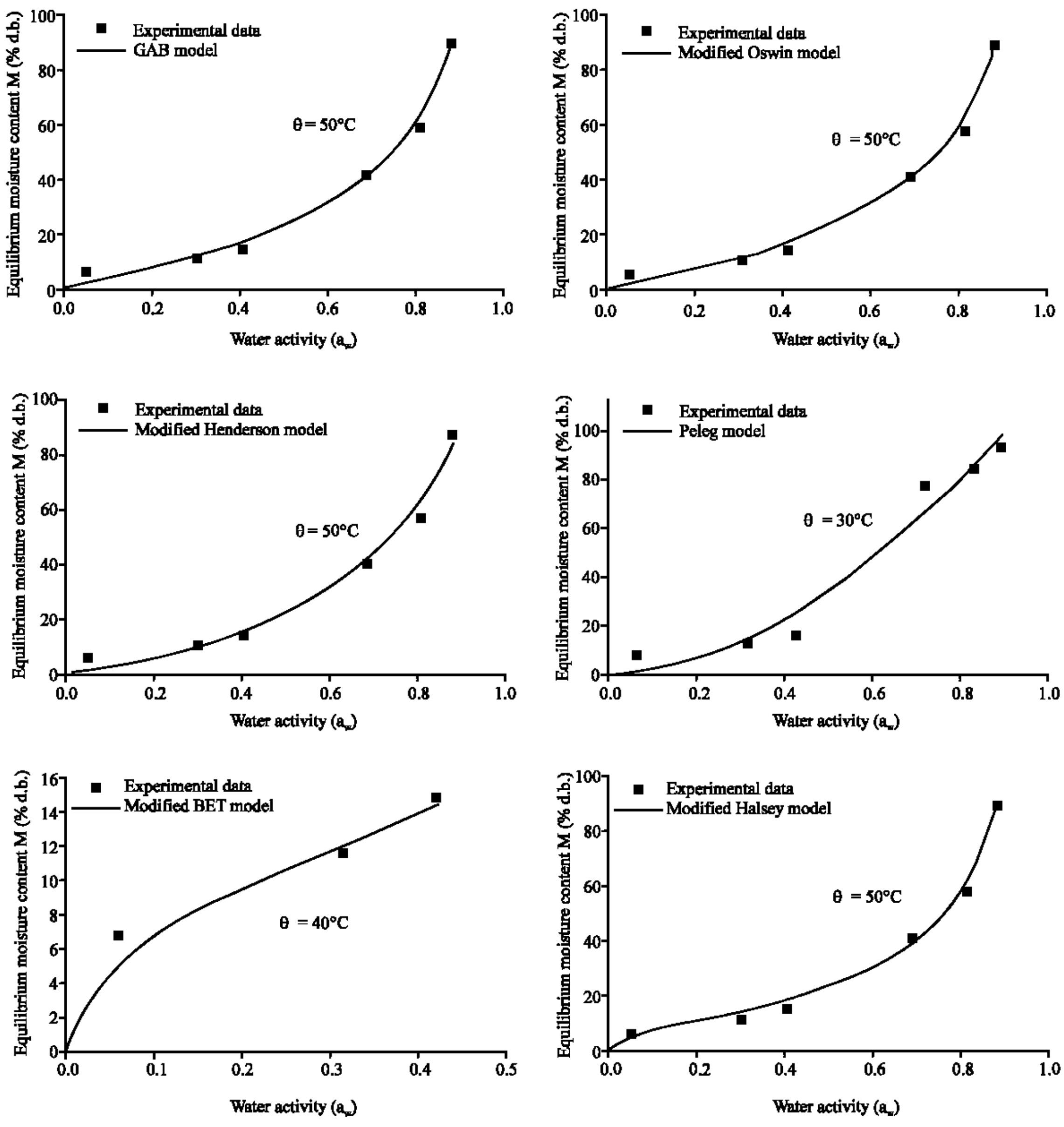

Fig. 11: Comparison of experimental and predicted adsorption equilibrium moisture contents of *Z. gaetulum* fitted by six models

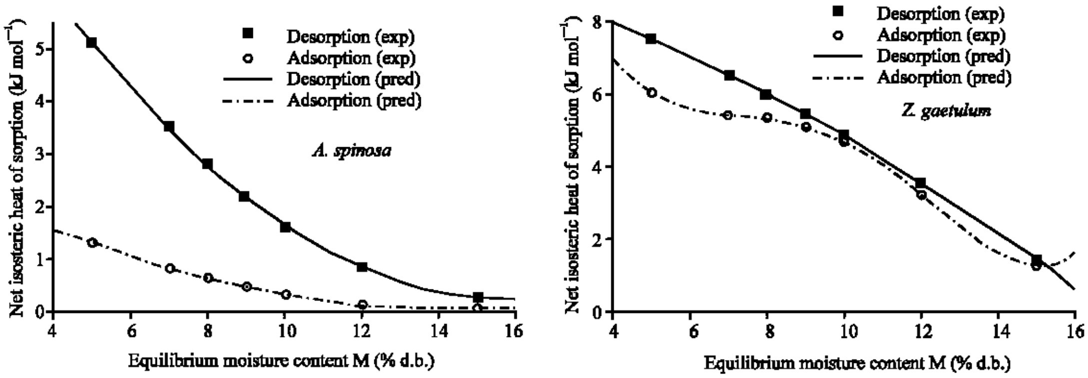

Fig. 12: Net isosteric heat of sorption for different equilibrium moisture contents

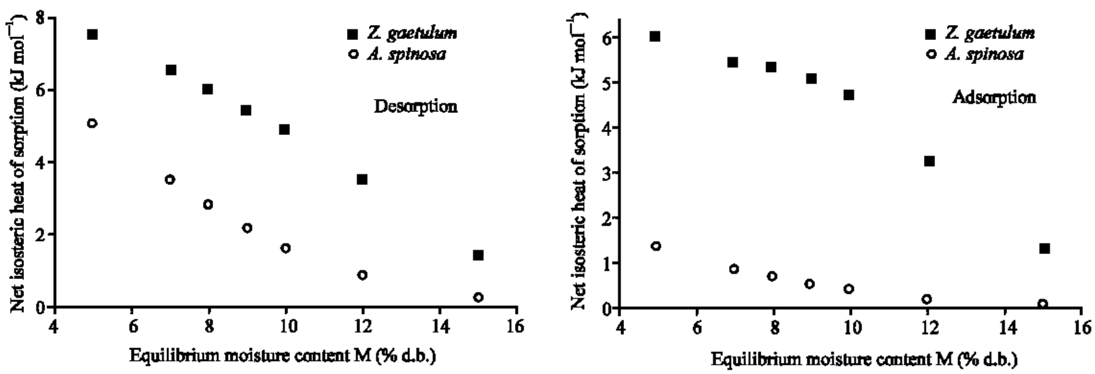

Fig. 13: Comparison of the net isosteric heats of sorption for two products at different equilibrium moisture contents

Vazquez *et al*., 2001). As shown in Fig. 12 and 13, isosteric heats of sorption are high at low moisture contents (<10%). In *A. spinosa*, the net isosteric heat of sorption decreased rapidly with an increase in material moisture content.

The net isosteric heat of desorption and adsorption of water in two plants can be expressed mathematically as a polynomial function of moisture content:

Zygophyllum gaetulum

$$\Delta h_d(des) = 9.3234\text{-}0.2668M\text{-}0.0204M^2\text{+}1.8890M^3 \quad (r = 0.9994)$$

$$\Delta h_d(des) = 22.2770\text{-}7.8009M + 1.3371M^2\text{-}0.0986M^3 + 0.0025M^4 \quad (r = 1)$$

Argania spinosa

$$\Delta h_d(des) = 10.5670\text{-}1.3084M\text{+}0.0414M^2 \quad (r = 0.9994)$$

$$\Delta h_d(des) = 2.9380\text{-}0.4025M + 0.014M^2 \quad (r = 1)$$

The differential entropy is plotted as a function of moisture content in Fig. 14. Once again the entropy data display a strong dependence on moisture content. The differential entropy of desorption and adsorption of water in two plants can be expressed mathematically as a polynomial function of moisture content:

Zygophyllum gaetulum

$$\Delta S_d(des) = \text{-}272.3011\text{+}90.7245M\text{-}8.2736M^2\text{+}0.1398M^3\text{+}0.0060M^4 \quad (r = 1)$$

$$\Delta S_d(des) = \text{-}1199.8501\text{+}474.2223M\text{-}63.5030M^2\text{+}3.5635M^3\text{-}0.0722M^4 \quad (r = 1)$$

Argania spinosa

$$\Delta S_d(des) = 199.1886\text{-}76.9336M\text{+}115678M^2\text{-}0.7768M^3\text{+}0.0193M^4 \quad (r = 1)$$

$$\Delta S_d(des) = 32.1906\text{-}13.1927M\text{+}1.9106M^2\text{-}0.1207M^3\text{+}0.0028M^4 \quad (r = 1)$$

Enthalpy-entropy compensation theory: The Δh_d and ΔS_d values for adsorption and desorption, at given moisture contents, were calculated by linear regression equation using Eq. 6. It was assumed that, at specific

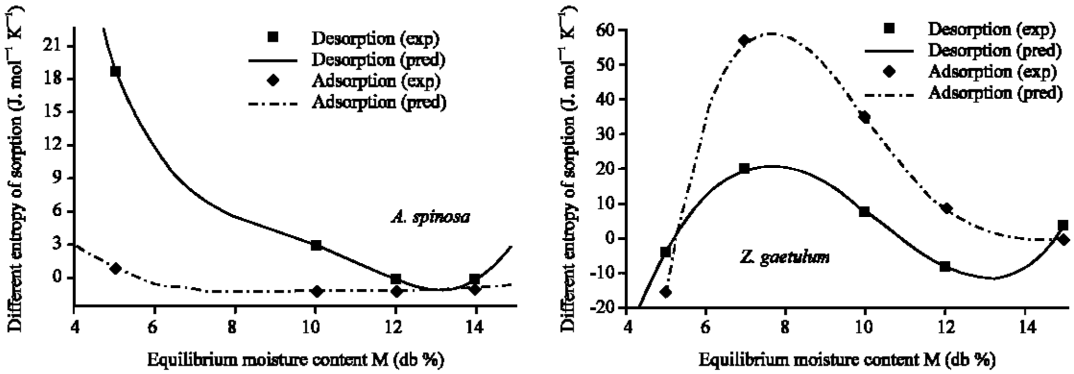

Fig. 14: Differential entropy of adsorption and desorption vs. equilibrium moisture content

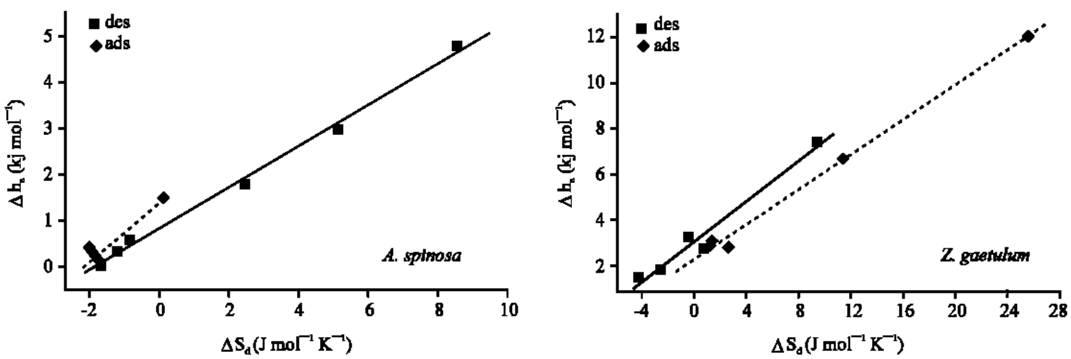

Fig. 15: $\frac{\Delta h_d}{\Delta S_d}$ relationship for adsorption and desorption for two products

Table 9: Characteristic parameters for Δh_d versus ΔS_d relationship

	T_β(K)	α (J mol^{-1})	r
Z. gaetulum			
des	437.05	2980.84	1
ads	378.41	2231.39	1
A. spinosa			
des	476.23	512.30	1
ads	671.41	977.38	1

moisture content, Δh_d and ΔS_d did not vary with temperature (Aguerre *et al.*, 1986; Simal *et al.*, 2007). The plot of Δh_d versus ΔS_d for each product (Fig. 15) shows a linear relation, with a coefficient of determination (r = 1); this indicates that compensation exists. The parameters T_β and α Eq. 7 were calculated from the data by linear regression and the values are shown in Table 9.

CONCLUSIONS

On the basis of this study the following conclusions can be drawn:

- The temperature has an important effect on sorption isotherms
- The equilibrium moisture content decreased with the increase in temperature at constant a_w
- The experimental results show that sorption isotherms of *A. spinosa* and *Z. gaetulum* have respectively a sigmoid shape (Type II) and (Type V)
- The thermal phenomenon of hysteresis was observed only for *A. spinosa* sorption isotherm. This is due to the fact that the moisture content of *Argan* almond at wet basis is very weak compared to that of *Z. gaetulum*
- *Z. gaetulum* isotherms are adequately described by the GAB and the modified Oswin equations. *A. spinosa* isotherms are adequately described by GAB and Peleg equations
- Net isosteric heats of sorption, calculated using the Clausius-Clapeyron equation, showed a power relation with moisture content; desorption values are higher than those for adsorption

- The heats of sorption increased with decreasing moisture content
- The heats of sorption of *Z. gaetulum* (healer plant) are higher than that of *A. spinosa* due to high water content
- The differential entropy of sorption can be characterized by a polynomial functions
- The isosteric heat versus entropy data satisfies the enthalpy-entropy compensation theory

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NOMENCLATURE

A, B, C, D	=	Model coefficients
ads	=	Adsorption
a_w	=	Water activity (dimensionless)
B_0, C_0, h_1, h_2	=	GAB coefficients
d.b.	=	Dry basis
des	=	Desorption
M	=	Equilibrium moisture content (% d.b.)
M_{ie}	=	Experimental equilibrium moisture content (kg kg^{-1} d.b.)
M_{ip}	=	Predicted equilibrium moisture content (kg kg^{-1} d.b.)
MRE	=	Mean relative error (%)
MSE	=	Mean square of error
R	=	Universal gas constant (J mol^{-1} K^{-1})
r	=	Correlation coefficient
T	=	Absolute temperature (K)
Δh_d	=	Net isosteric heat of sorption (kJ mol^{-1})
θ	=	Temperature in (°C)

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